

## ASPHALTENES FROM COAL LIQUEFACTION

F. K. Schweighardt, H. L. Retcofsky and R. Raymond

Pittsburgh Energy Research Center, U. S. Energy Research and  
Development Administration, 4800 Forbes Ave., Pittsburgh, PA 15213

### INTRODUCTION

Asphaltenes are considered to be one of the principle intermediates in the conversion of coal to an oil product. But, over the past four decades, investigations of coal hydrogenation have only used a simple operational definition of coal-derived asphaltenes - "Benzene soluble and hexane insoluble". What then can be said about these asphaltenes? What is the established laboratory procedure for isolating asphaltenes? What steps have been taken to characterize and compare asphaltenes generated from different coal liquefaction processes? Do the asphaltenes affect the physical and/or chemical properties of a coal-derived oil? These and many other questions need to be studied and some kind of answer proposed. Recent investigations indicate that asphaltenes contribute to a large measure to the viscosity of the product oil. It has even been suggested the asphaltenes are the coal monomer - the smallest unit of coal that still retains, to some degree, the spectral qualities of the whole coal. Before we go further we must establish isolation techniques that are standardized, and that do not chemically affect the asphaltene components. Once free from the virgin coal-derived oil what then are the physical, chemical and spectral properties of these "Benzene soluble-hexane insoluble" materials we call asphaltenes. When these questions have been investigated, then we may be able to answer -

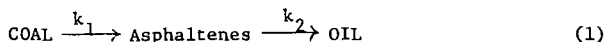
What are asphaltenes?

### IN THE BEGINNING

As far back as 1942 German scientists involved in coal conversion products wrote a "summary report on experiments performed at Scholnen to establish a suitable method for asphalt analysis". (1) In these early investigations the benzene soluble-hexane insoluble material was referred to as asphalts. (2,3) But, at the U. S. Bureau of Mines, the term asphalt was considered objectionable because the same word was commonly used to describe a petroleum-derived product. The petroleum product differs in some rather important aspects from coal-hydrogenation material as will be shown.

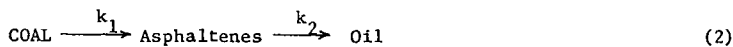
Therefore, in the United States about 1950-51, the term asphaltenes was used to define the benzene soluble-hexane insoluble components of coal-conversion products. Weller, et al. (4) detailed the isolation of the asphaltenes and, with some general modifications (5) this method has been used at the Pittsburgh Energy Research Center on a large number of samples. Recently Sternberg, et al. (6) proposed a slightly different version of separating asphaltenes from SYNTHOIL (7) centrifuged liquid products (CLP).

Let us go back to the late 1940's and early 1950's when mechanisms were first suggested for the hydrogenation of coal. Weller, et al. (4) determined that the conversion of coal to oil involved two consecutive first order reactions,



At 400° C  $k_1$  was reported as 25 times larger than  $k_2$ .

More recently Lieberberg and Potgieter (8) derived a more complex mechanism which includes the following simultaneous and consecutive reactions:



Markov and Orechhin (9) on the other hand have proposed that in the initial stages of coal hydrogenation it is not the asphaltenes that are formed first, but a substance that is insoluble in benzene yet soluble in pyridine. Sternberg et al. (6) have separated these materials according to their isolation scheme and have termed these pyridine soluble-benzene insoluble materials "preasphaltenes". Now we have not only asphaltenes to contend with, but preasphaltenes as well. That brings us to one of our earlier questions - what effect do asphaltenes have on the physical properties of coal-derived oils. Figure 1,

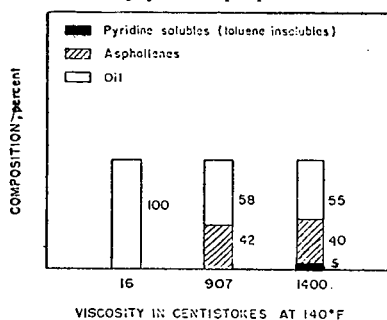


Figure 1. Effect of pyridine solubles (toluene insolubles) and asphaltenes on viscosity.

from work by Sternberg, et al. (7) shows in at least one case that the viscosity of a SYNTHOIL CLP is effected by the presence of asphaltenes and preasphaltenes. Why the effect is so large is still a matter of investigation.

#### ASPHALTENE ISOLATION

Before going any further we should account for the isolation of asphaltenes. Figure 2 gives

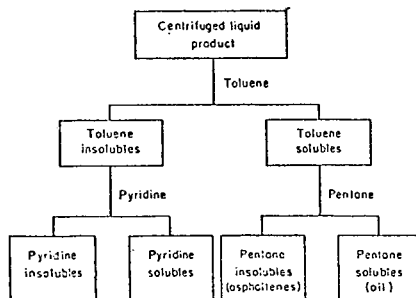


Figure 2. Fractionation scheme for centrifuged liquid product (CLP).

the fractionation scheme for asphaltenes from a SYNTHOIL CLP. The initial product as received from the process stream is hot. It is placed in a jar, quickly flushed with nitrogen, and allowed to cool to room temperature in the closed container. A portion of the sample is subjected to the isolation procedure as soon as it attains room temperature. The initial separation removes the benzene (10) insolubles. This can be accomplished by centrifugation on an analytical scale (1-3 grams), or by the Soxhlet method on a preparative scale (10-20 grams).

The recovered benzene insolubles (BI) can then be subjected to pyridine extraction to give pyridine insolubles (ash content  $\approx 80\%$ ) and pyridine solubles (preasphaltenes). The benzene soluble portion of the CLP is reduced in volume by nitrogen flush at 30-35° C on a water bath until an approximate volume ratio of 1:1 benzene/solubles is reached. We now propose the use of n-pentane (pesticide grade for all solvents) to precipitate the asphaltenes. Pentane is added with rapid stirring, or mild (50 watt) sonication, to precipitate the asphaltenes. If a preparative method is used, a fine double thickness thimble is required, or three pentane washings on the analytical scale, with centrifugation at 2500 rpm at 20° C for 15 minutes. The asphaltenes are collected and dried at 65° C in vacuo to constant weight or redissolved in benzene (1 gram asphaltene/5 ml benzene) and freeze-dried. The later technique gives a fine, light tan material. All final products should be stored at -40° C in a glass sealed container.

The asphaltenes and preasphaltenes can be further separated by the method of Sternberg et al., (11) Figure 3. The asphaltenes are dissolved in benzene (1 gram/20 ml

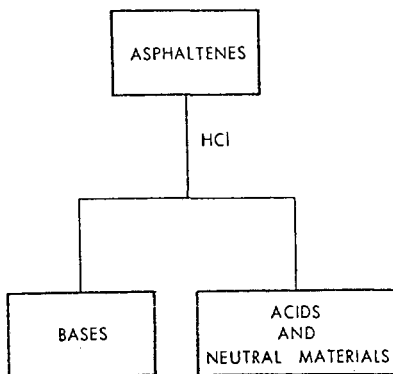


Figure 3. Asphaltene fractionation scheme.

benzene), centrifuged to collect any undissolved material, then dry HCl gas is slowly bubbled through the solution until no further evidence of precipitation is observed. This procedure forms an HCl adduct with the basic heterocyclic nitrogens ( $-N=$ ). In the solution remain the neutral and acidic compounds which can be recovered by reducing the benzene volume with a nitrogen purge and freeze-drying the final solution. The nitrogen adduct can be freed of HCl by back titration in benzene with 0.5 N NaOH. This is best achieved with a freshly prepared base adduct. Prolonging this last step increases the amount of benzene insolubles left after back titration.

We have outlined these methods in some detail because, as of today, there is no standardized method for separating asphaltenes. In many cases the yield of asphaltenes can vary as much as 50% and the benzene insolubles as much as 100% by just changing the laboratory technique.

Our method may not be the best, but we find it to be reproducible to within 3%, and by using centrifugation techniques losses are less than 2% because only solutions are transferred.

#### CHARACTERIZATION OF ASPHALTENES

Husack and Columbic (12) first described a separation scheme for the characterization of the phenolic constituents of coal-derived asphaltene by extracting with aqueous alkali and methanolic KOH (Classen alkali). They concluded that most of the oxygen content of the phenolic fractions could be accounted for by hydroxyl (OH) and that 25% added active hydrogen could be assigned to nitrogen compounds (NH). Sternberg et al. (11) some 25 years later came to the same conclusions by separating the acidic and basic components by HCl adduct formation and determining the presence of phenols, pyrroles and pyridine-like bases by thin-layer chromatography (TLC), thin-layer electrophoresis (TLE) and nuclear magnetic resonance (NMR). Sternberg has proposed that the acidic and basic components form a macro-molecular hydrogen-bonded complex upon the addition of pentane to the aromatic solution. Schweighardt, et al. (13) have investigated this hydrogen bonded complex by multi-nuclei magnetic resonance ( $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{14}\text{N}$ ), and have confirmed that the separable acid and base components do form hydrogen bonded species with model compounds (pyridine and o-phenylphenol), as well as with each other.

The presence of phenolic (OH) functional groups in the asphaltene fraction of coal hydrogenation oils has been of considerable interest over the past 20 years. Friedman, et al. (14) were the first to quantitate the hydroxyl content by forming the trimethylsilyl ether (TMS) of the asphaltene. The infrared analyses of the product indicated that almost all the hydroxyl groups had reacted. Their treated asphaltene contained 6.21% silicon, corresponding to a hydroxyl oxygen content equivalent to 64% of the oxygen present in the original asphaltene.

Brown, et al. (15) have applied the TMS derivative formation to the acid and base fractions of a SYNTHOIL asphaltene and have confirmed the presence of hydroxyl (OH) by infrared and nuclear magnetic resonance. An important feature of their work is that in dilute solution ( $\text{CS}_2$ ) the base components of a coal-derived asphaltene contain some OH, as evidenced in the infrared spectrum in figure 4. The OH content was confirmed by forming a

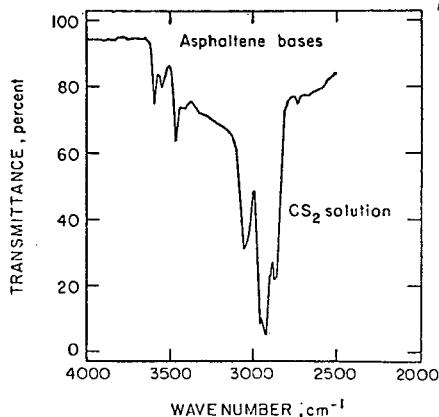


Figure 4. Infrared spectrum of asphaltene bases

TMS derivative and observing the disappearance of the OH bands at 3560  $\text{cm}^{-1}$ . The exact nature of these hydroxyls is in question.

Sternberg, et al. (11) stated that they could not detect phenolic OH in the base fraction after TLC and TLE analyses. The base component of Brown, et al. (15) was also tested by TLC and spray reagents and a strong confirmation of phenolic OH was not detected. It is possible that these OH are not phenolic, but more alcoholic in nature, therefore, a positive phenolic test was not observed. Another possibility is that the OH are so hindered that the phenolic reagent could not form its derivative. It is no wonder that many more interesting questions are being proposed than are being answered.

Nuclear magnetic resonance (NMR) has been used to a much greater extent recently due to the advent of computer processing of the signal for enhanced signal-to-noise ratio. We have used both  $^{13}\text{C}$  and  $^1\text{H}$  NMR to determine aromaticity (16) of coal hydrogenation products as well as asphaltenes. An interesting preliminary set of experiments was made for the use of a stable isotope tracer,  $^2\text{H}$ -deuterium. (14) Another such experiment was made in an autoclave with fresh coal and an asphaltene-free partially deuterated vehicle oil, run at  $450^\circ\text{C}$  and pressurized with nitrogen gas in place of hydrogen. If the resulting new asphaltenes, generated from the fresh coal, were found to contain incorporated deuterium, as evidenced by its  $^1\text{H}$  NMR resonance being greater than natural abundance, then a deuterium transfer could possibly have taken place between the vehicle oil and the coal. Our initial results indicate a slight uptake of deuterium, with some specificity at the aliphatic carbon positions. Work in this area, using stable isotope labels, is continuing and should provide some needed insight into the mechanism of hydrogen transfer in coal liquefaction.

#### SUMMARY

Over the past 40 years of coal liquefaction, a product that is benzene soluble and n-pentane insoluble, now referred to as asphaltenes, has provided some very interesting questions. We have only touched upon a few of the highlights in the history, isolation, and characterization of these asphaltenes in this presentation. What then is an asphaltene is still an unanswered question. We have yet to establish a standard asphaltene isolation method, hence, only generalization can be made about the final product. Asphaltenes and preasphaltenes might well be the smallest units into which coal may be divided and yet still retain most of the spectral and some of the chemical properties of the original whole coal.

It is therefore not so surprising that we cannot answer the question -

"What are asphaltenes?" .....at this time.

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